EGVI

European Green Vehicles Initiative

STABLE

STable high-capacity lithium-Air Batteries with Long cycle life for Electric cars

September 2012 / August 2015

Coordinator Silvia Bodoardo: silvia.bodoardo@polito.it

Overview

THEME [GC.NMP.2012-1] Innovative automotive electrochemical storage applications based on nanotechnology

Grant agreement for: Collaborative project

Project acronym: **STABLE**

Project full title: “Stable high-capacity lithium-Air Batteries with Long cycle life for Electric cars”

Grant agreement no: 314508

Eu contribution: 2,495,517.00 euros

Duration : 3 years. 1 September 2012- 31 August 2015

Partners

POLITECNICO DI TORINO (POLITO) - ITALY	UNIVERSITY COLLEGE CORK, NATIONAL UNIVERSITY OF IRELAND, CORK (UCC) - IRELAND
ACONDICIONAMIENTO TARRASENSE ASSOCIACION (LEITAT) - SPAIN	SAKARYA UNIVERSITESI (SAU) - TURKEY
L'UREDERRA, FUNDACION PARA EL DESARROLLO TECNOLOGICO Y SOCIAL (LUREDERRA) - SPAIN	CELAYA,EMPARANZA Y GALDO INTERNACIONAL, S.A. (CEG) - SPAIN
SWEREA IVF AB (IVF) - SWEDEN	ELAPHE, Elaphe Propulsion Technologies Ltd (Elaphe) - SLOVENIA

Scenario

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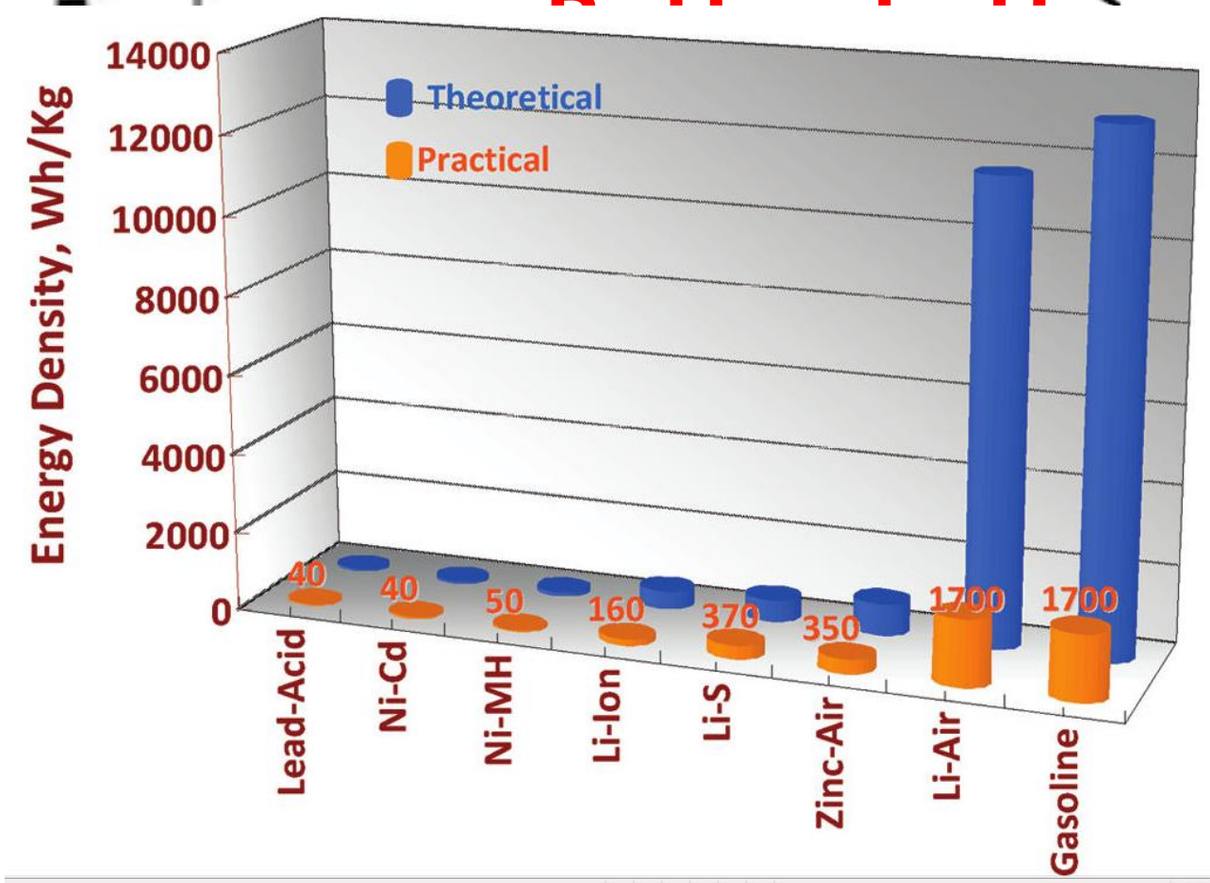
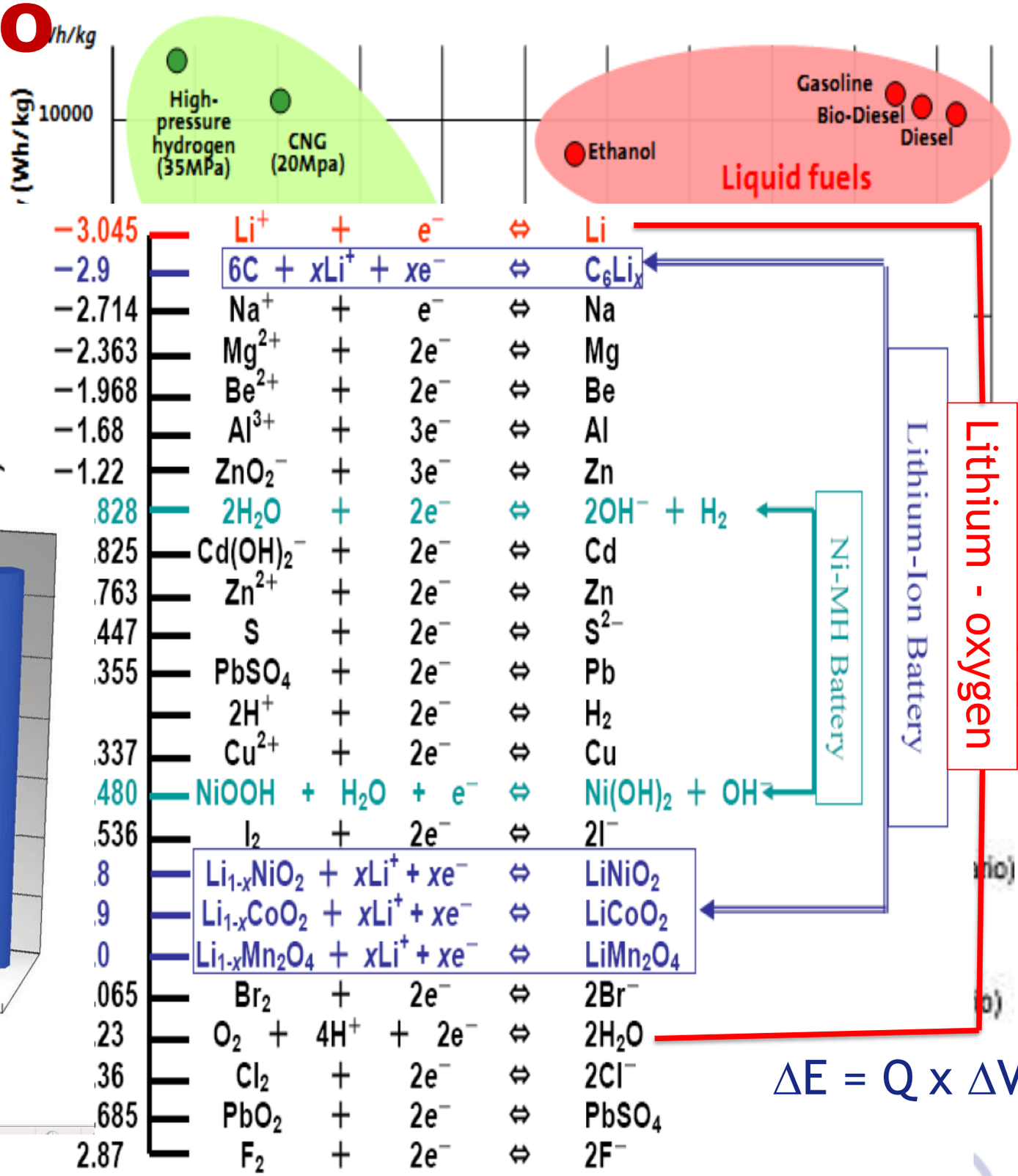
World: Electric vehicle p
electric vehic

More batte



IBM source



$\Delta E = Q \times \Delta V$

Life Cycle Assessment

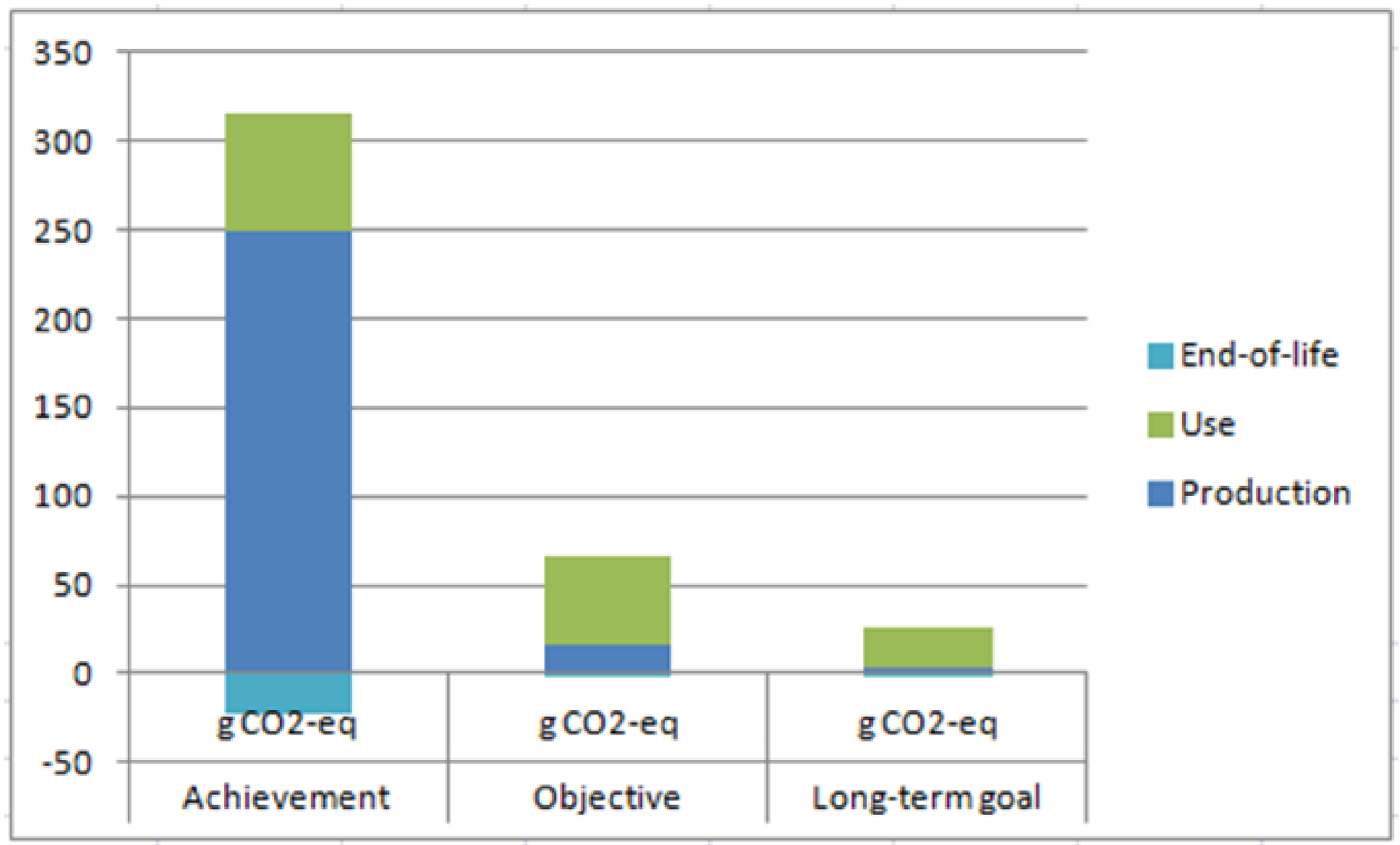
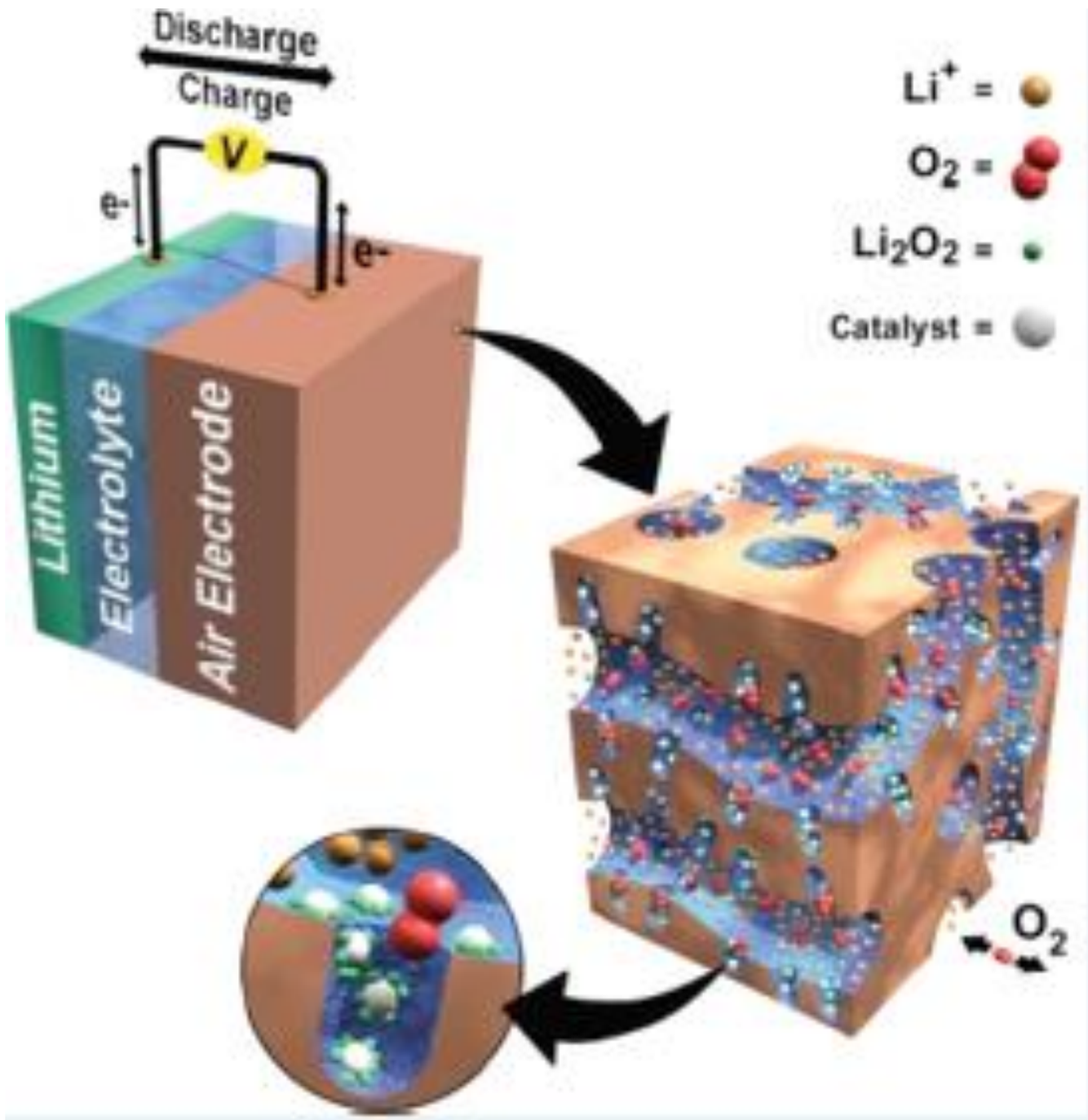


Figure 19 Climate impact per vehicle km for the different scenarios

The Li-air battery



Nonaqueous:

$2Li^+ + 2e^- + O_2 \leftrightarrow Li_2O_2$

$E_0 = 2{,}96V$ vs Li^+ / Li

ORR:

$$O_2 + e^- \rightarrow O_2^-$$

$$O_2^- + Li^+ \rightarrow LiO_2$$

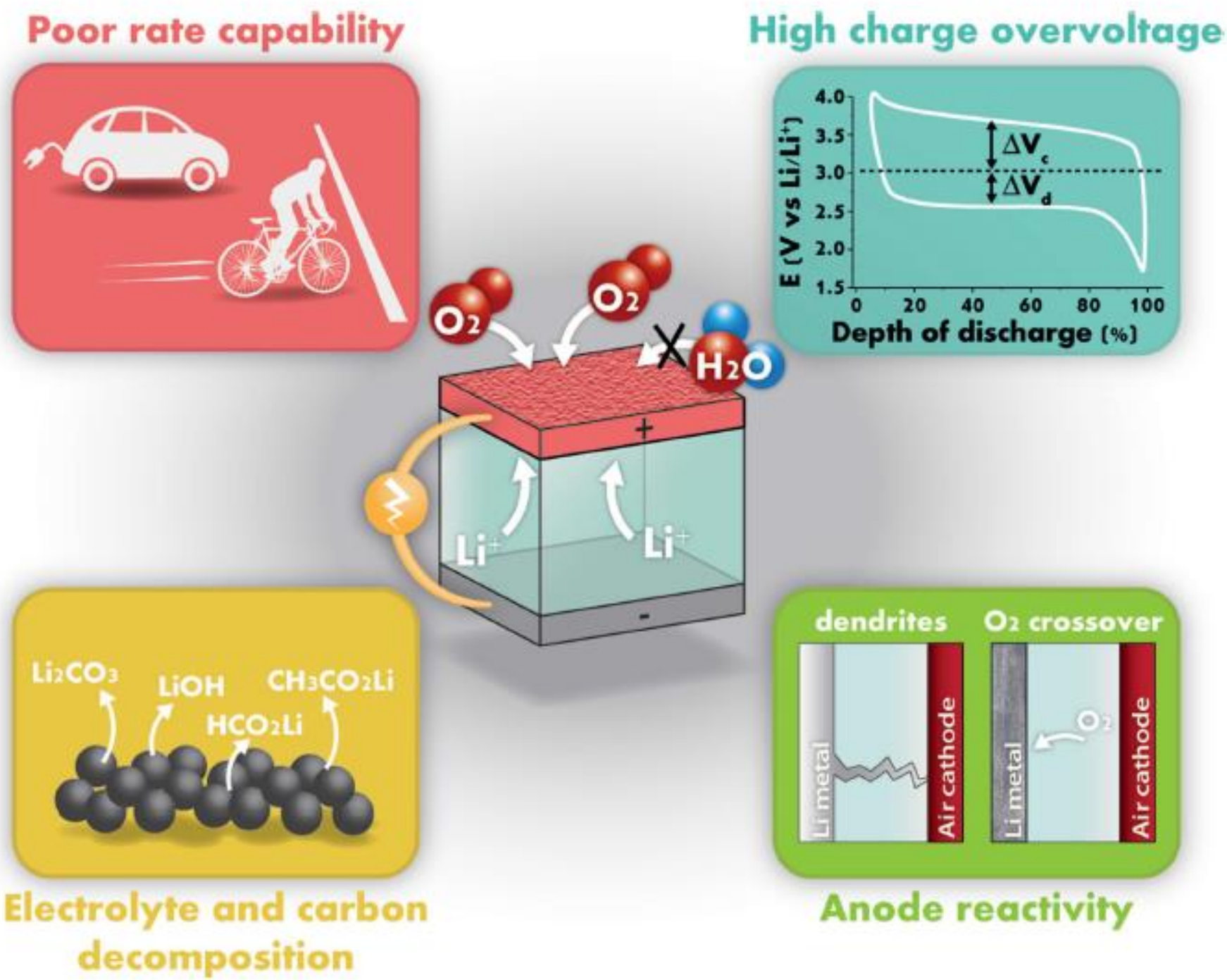
$$LiO_2 \rightarrow Li_2O_2 + O_2$$

OER:

$$Li_2O_2 \rightarrow 2Li^+ + O_2 + e^-$$

Y. Shao, S. Park, J. Xiao, J-G. Zhang, Y. Wang, J. Liu, ACS Catal., ***2012****, 2, 844-857*

Problem statement



By courtesy of Bruno Scrosati

L. Grande, E Paillard J. Hassoun, J-B Park, Y-J Lee, Y-K Sun, S. Passerini, B. Scrosati, Adv. Mater. ***2015****, 27, 784-800*

STABLE's OBJECTIVES

- Improve Li-air battery cells through innovations of battery anode, cathode, electrolyte materials and technologies, and assembly of battery cells:
  - high capacity > 2000mAh/g
  - cycle life improvement to 100-150 cycles
  - positive impact on battery performance, cost and environment

SEVENTH FRAMEWORK PROGRAMME

STABLE

General organization

Simulation and modeling, LCA

Synthesis and optimization of **ANODE** materials

Synthesis and optimization of **ELECTROLYTE** materials

Synthesis and optimization of **CATHODE** materials

Assembly and optimization of **complete Li-air cell**

Coordination and dissemination

cathode

- carbon based cathodes
- materials with or without catalyst
- free standing cathodes
- as ink on carbon based cathodes
- Study and realization of protective membranes to reduce the water inlet

cathode

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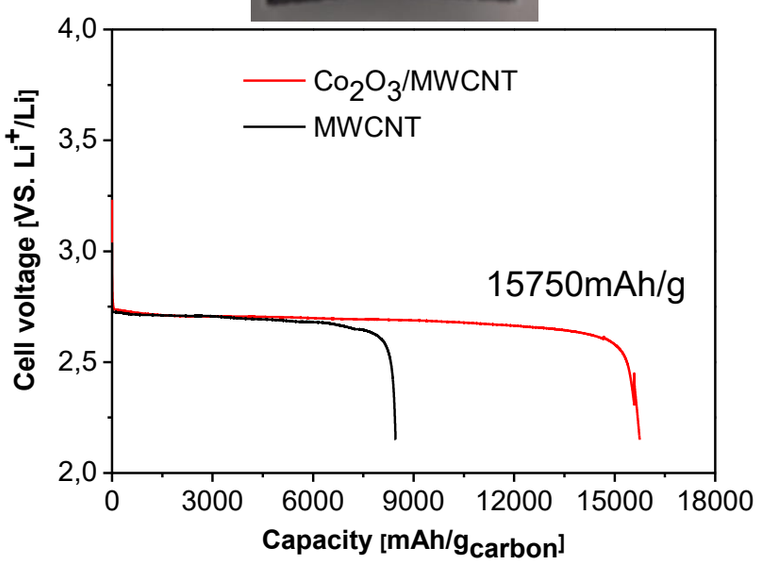
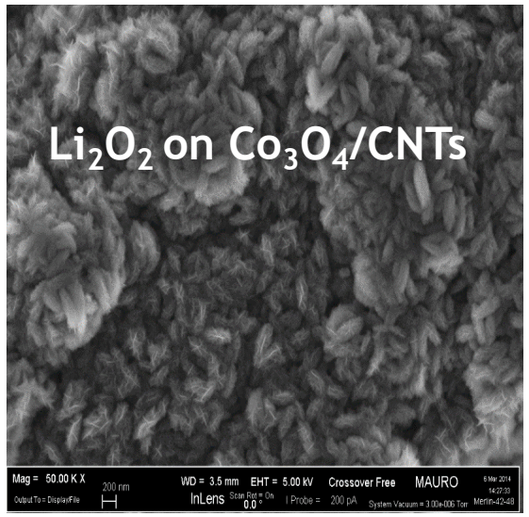
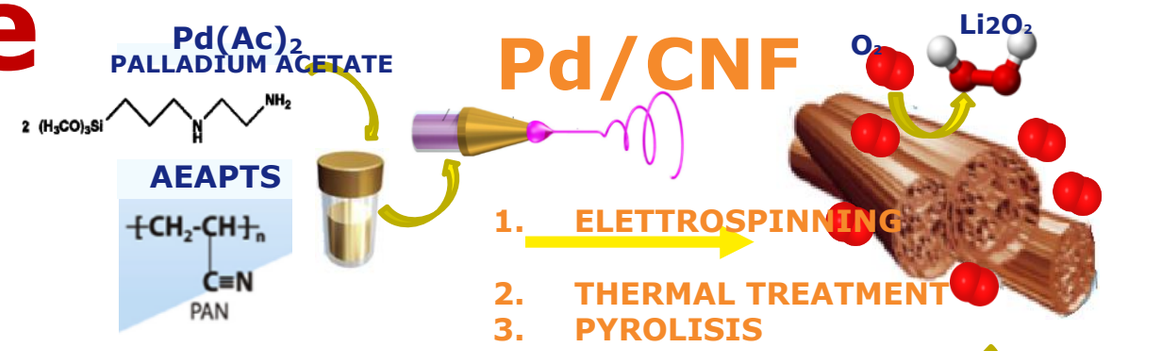
SYNTHESIS by FSP of MnO_2- Co_3O_4 NANOPARTICLES for INKS

Lurederra centro tecnológico





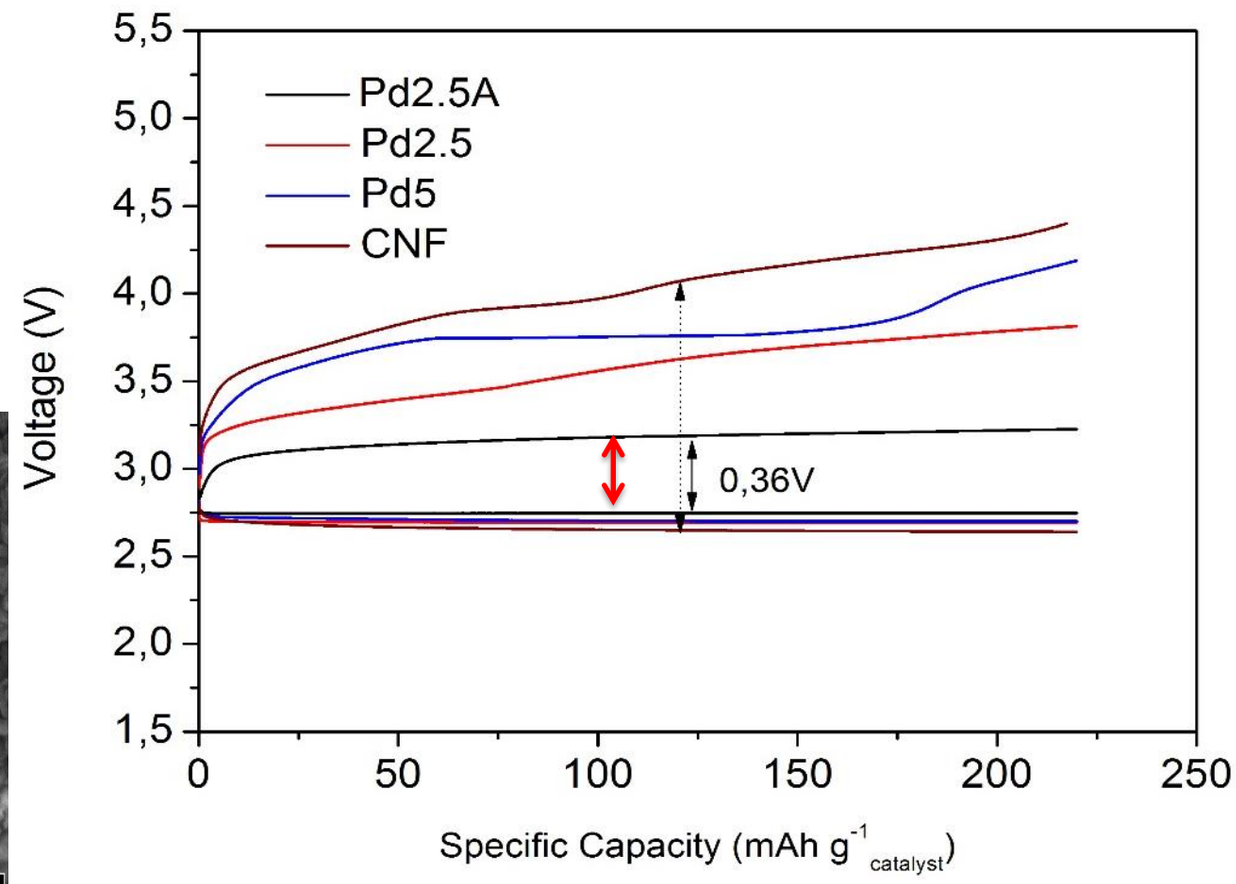
HIGH CAPACITY CATHODE 15700 mAh/g



Metal catalysts the effect of Pd

Overpotential reduction

LEITAT managing your technologies

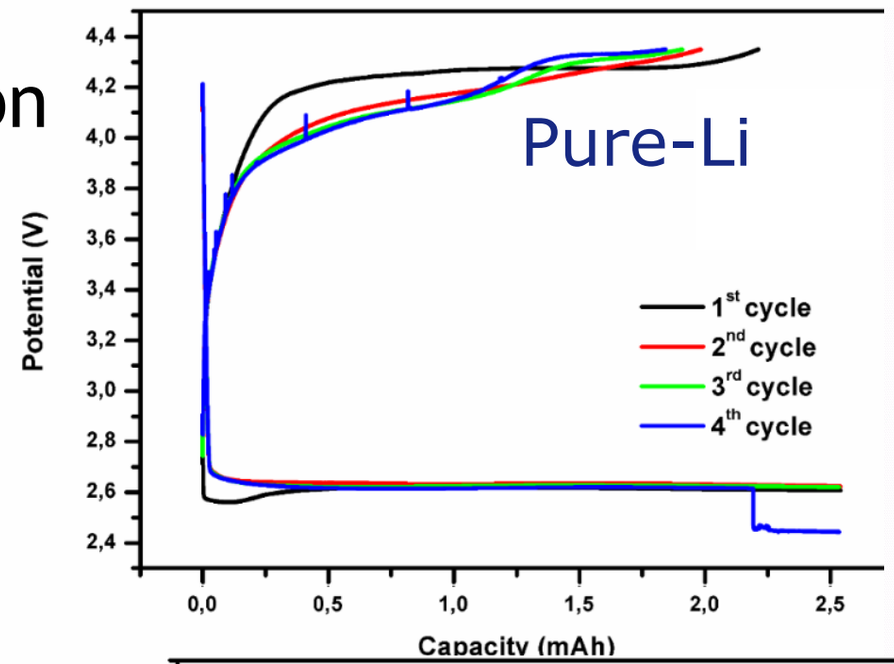


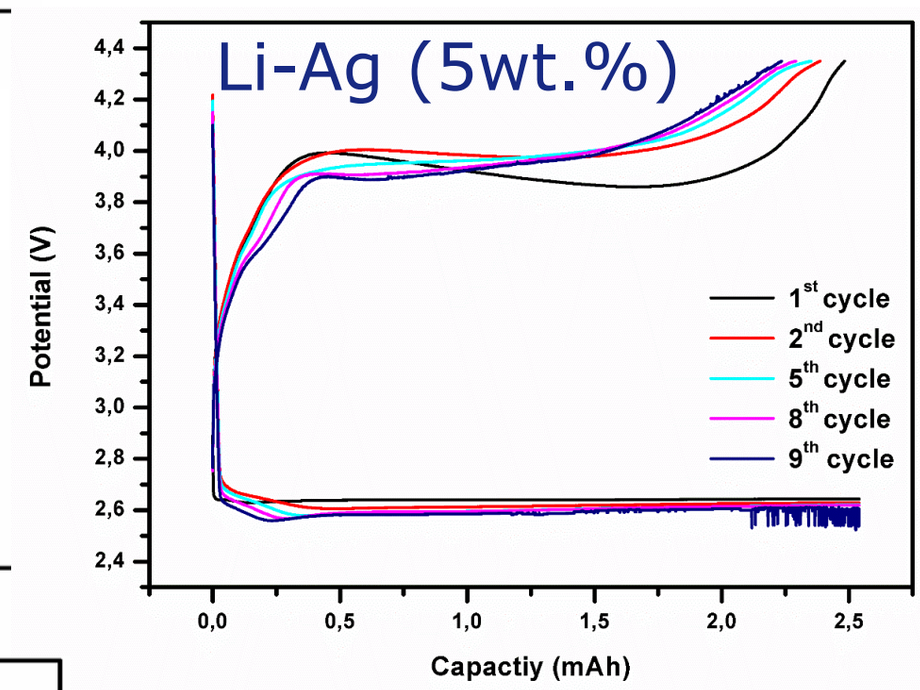
Cathode: CNFs or Pd/CNFs, binder PVDF Kynar (90:10) on GDL24BA (Sigraget)
Anode: Lithium foil 2,54cm^2
Electrolyte: TEGDME/$LiClO_4$
Continuous O_2 flow 3.5ml/min
Applied current: 20mA/g
10h discharge/10h charge

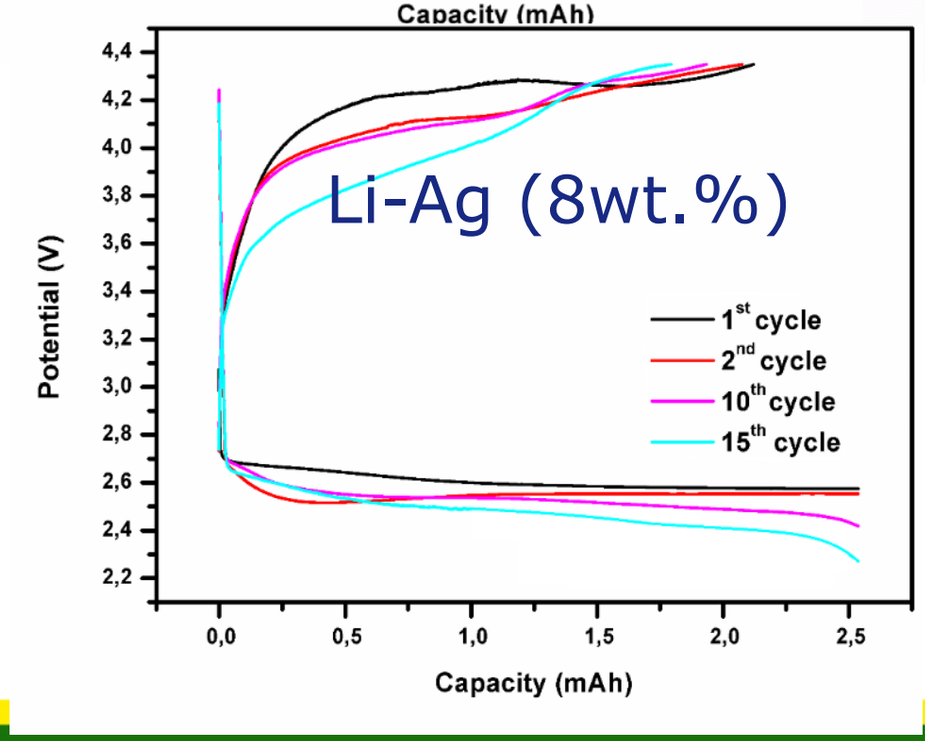
anode

Different strategies:

- Li protection
- Alloys production (Mg and Ag)







1 M LiPF6 in TEGDME as electrolyte and GDL (gas diffusion layer) as cathode and prapered lithium-silver alloys were used as anode.

electrolyte

Organic solvents:

- Carbonate-based solvents (EC, DEC, PC)
- Tetraethylene glycol dimethy lether (TEGDME)
- N-methyl-2-pyrrolidone (NMP)
- Dimethyl sulfoxide (DMSO)

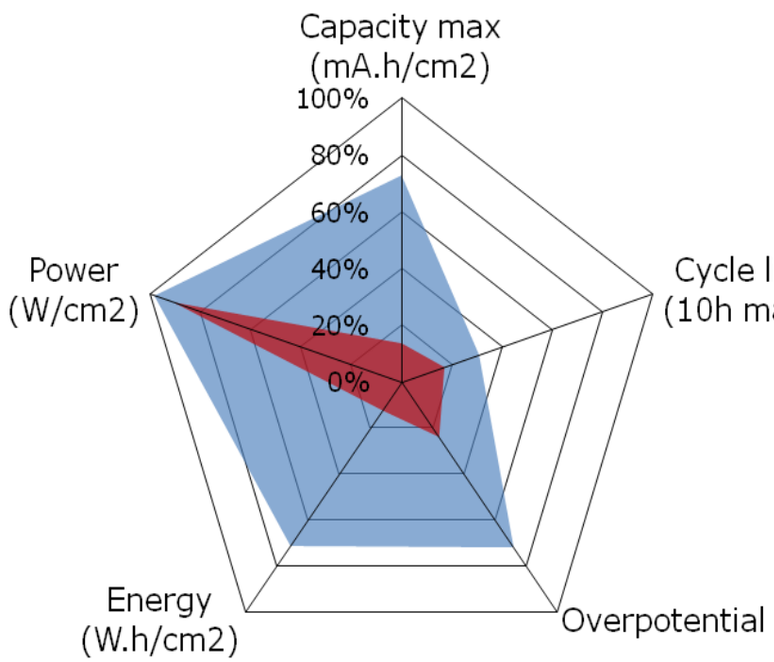
Ionic liquids (ILs):

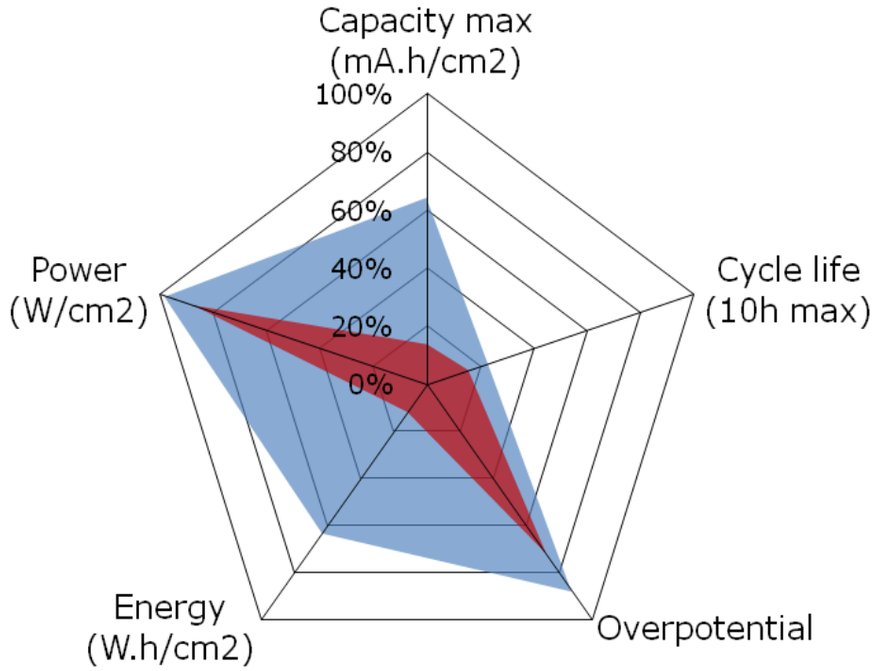
- cation: imidazolium, pyrrolidinium, piperidinium
- anion: bis(trifluoromethylsulfonyl)imide, hexafluorophosphate

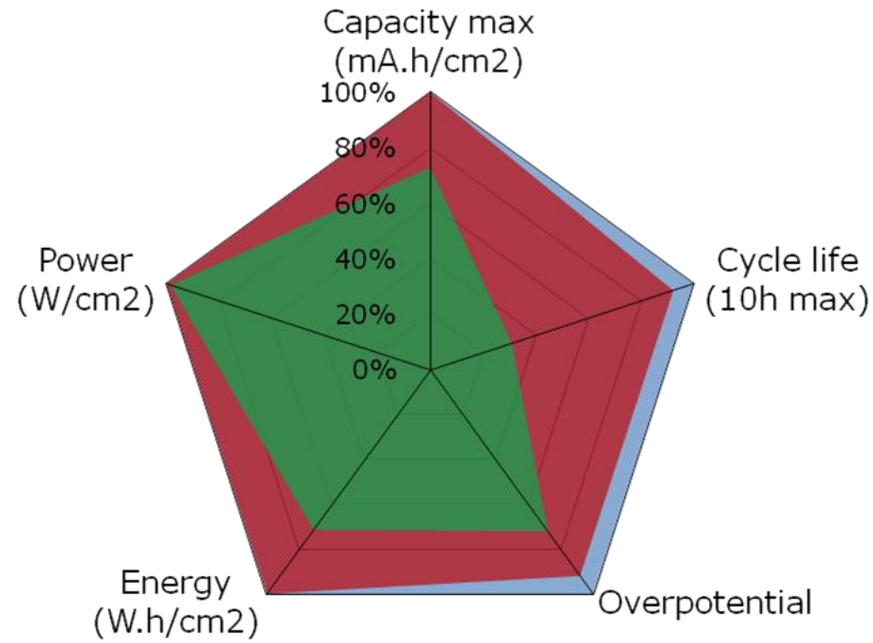
Mixture ILs + organic solvent

Additives: Nanoparticles of CeO_2, ZrO_2, SiO_2, Al_2O_3, TiO_2

Electrolyte
(Summary)







D3.1 (M1-M12)

- TEGDME + 0.5wt% $LiClO_4$
- EMI TFSI+ 0.5wt% $LiClO_4$

D3.2 (M13-M24)

- NMP + $LiPF_6$ + PeO + Al_2O_3
- EMI TFSI+ LiTFSI + PeO

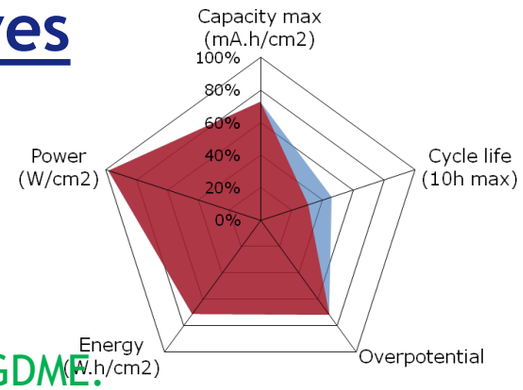
D3.3 (M25-M32)

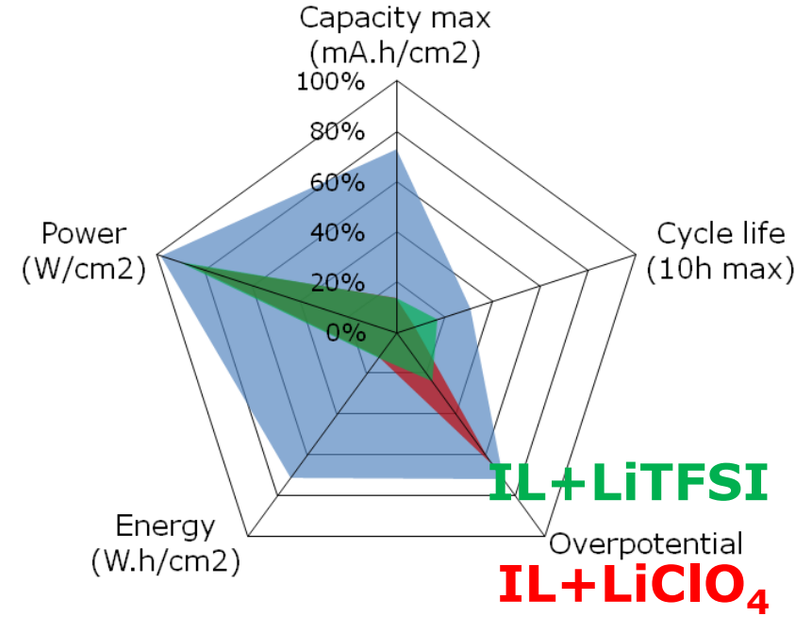
- EMI TFSI:DMSO (20:80wt%) + 0.5wt% $LiClO_4$
- DMSO+ 0.5wt% Al_2O_3 + 0.5wt% $LiClO_4$
- TEGDME + 0.5wt% $LiClO_4$

electrolyte

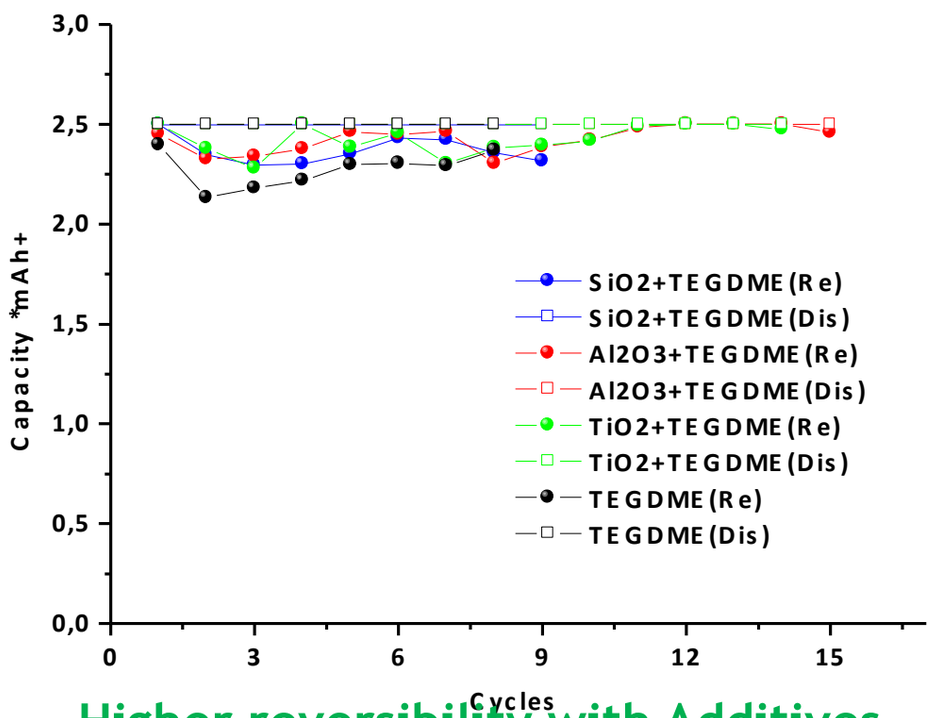
Organic solvents + additives

$LiNO_3$





Capacity with and without additive in TEGDME:

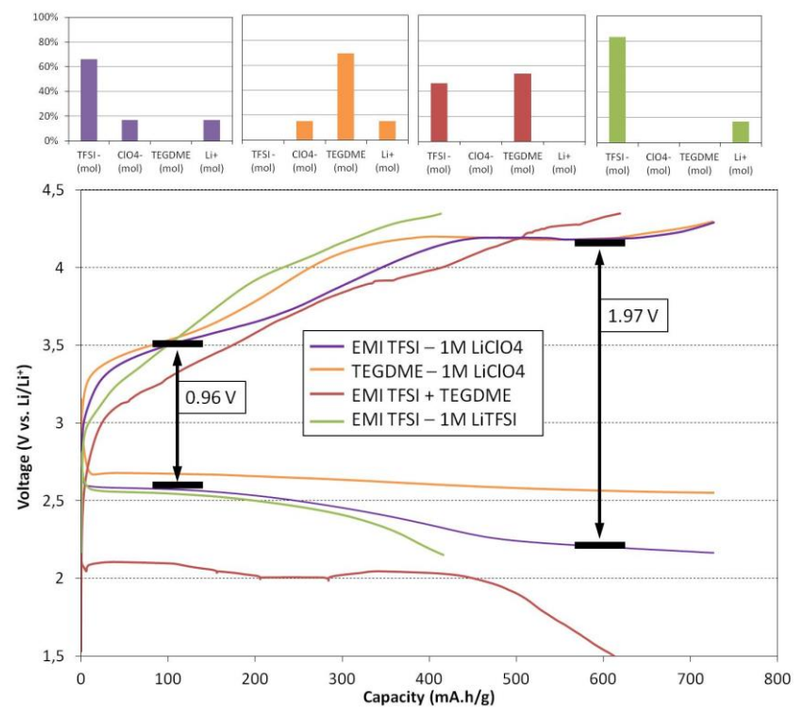


Higher reversibility with Additives

Capacity for charge and discharge are closer with additives

Coulombic efficiency is higher

$TEGDME+$
$LiClO_4$



Higher reversibility with $LiClO_4$ salt

2 plateaus observed with:

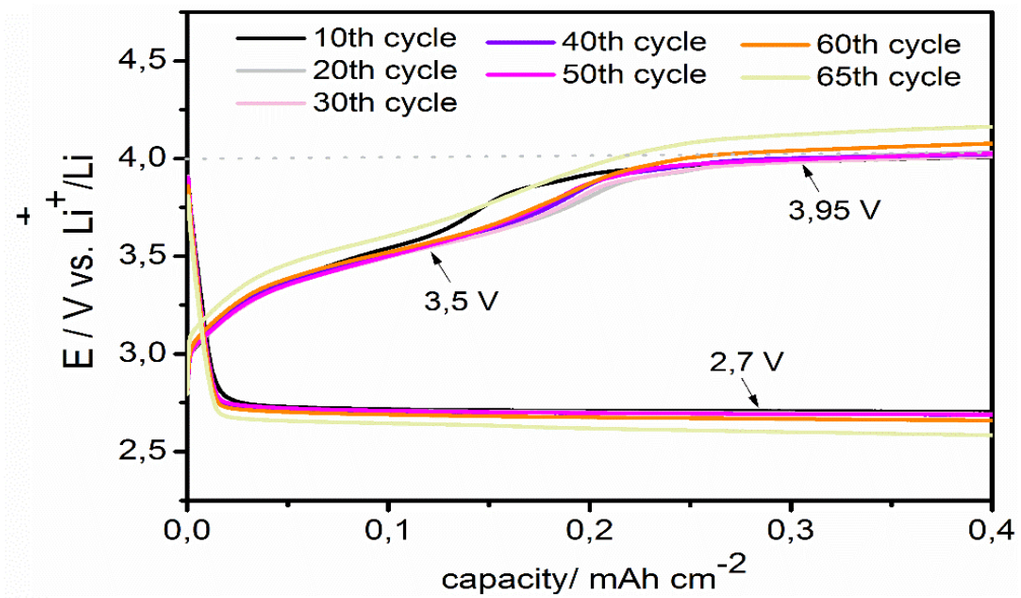
- EMI TFSI-1M LiClO4
- TEGDME-1M LiClO4

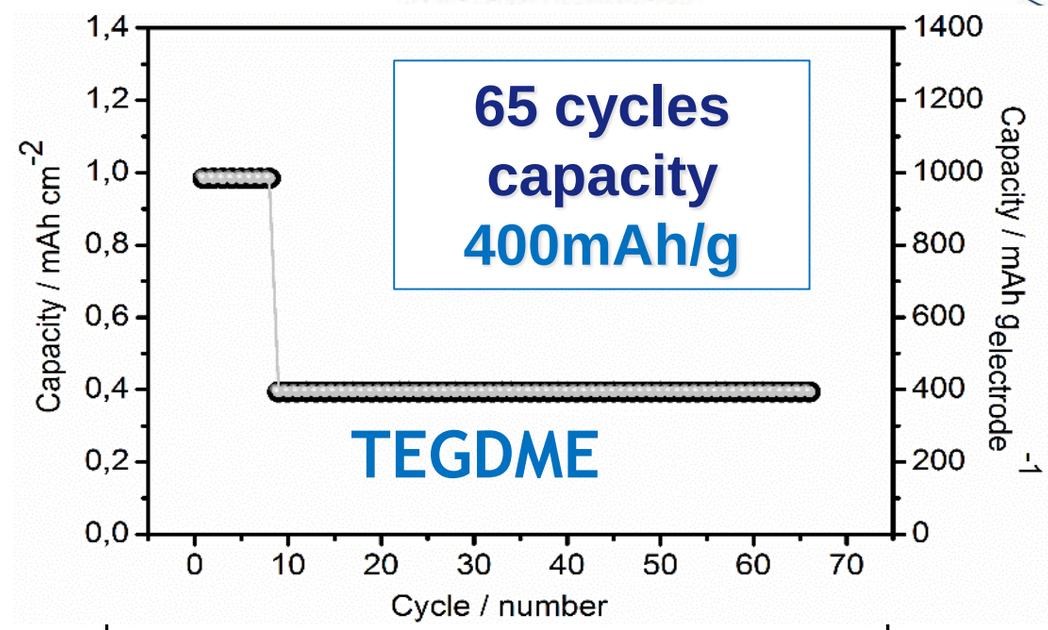
→ 2 reactions: dissolution of 2 by-products

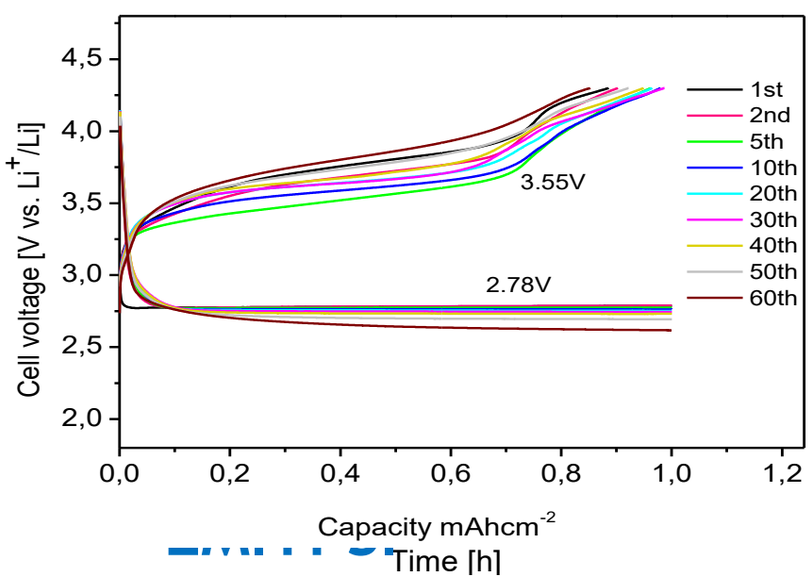
Organic solvents / ionic liquids

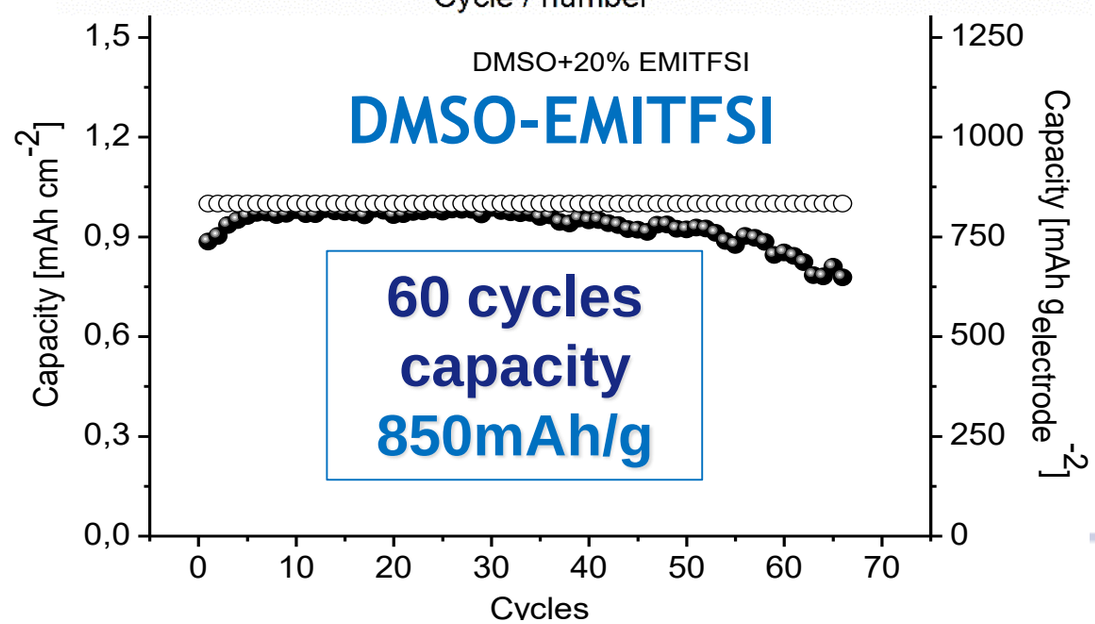
Cathode/electrolyte interaction

INKS on GDL24BC with MESOPOROUS Co_3O_4









Test of cathode material: INKS ON GDL 24BC + MESOPOROUS Co_3O_4

ECC-Air (EL-Cell); Anode: Li foil Electrolyte: TEGDME – 0.5M $LiClO_4$;

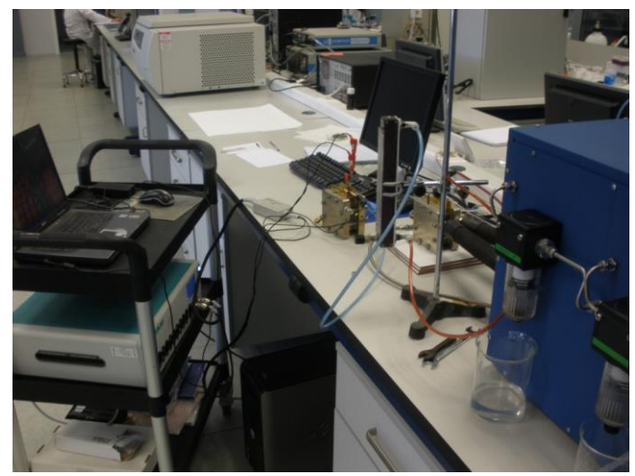
O_2 : 3.5 mL/min; 0.1mA/cm^2, 2.15-4.35V, 10h max.

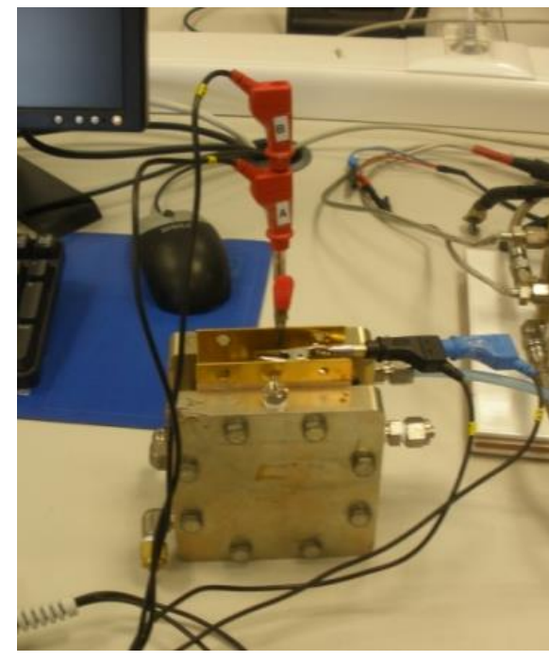
Prototype - High capacity

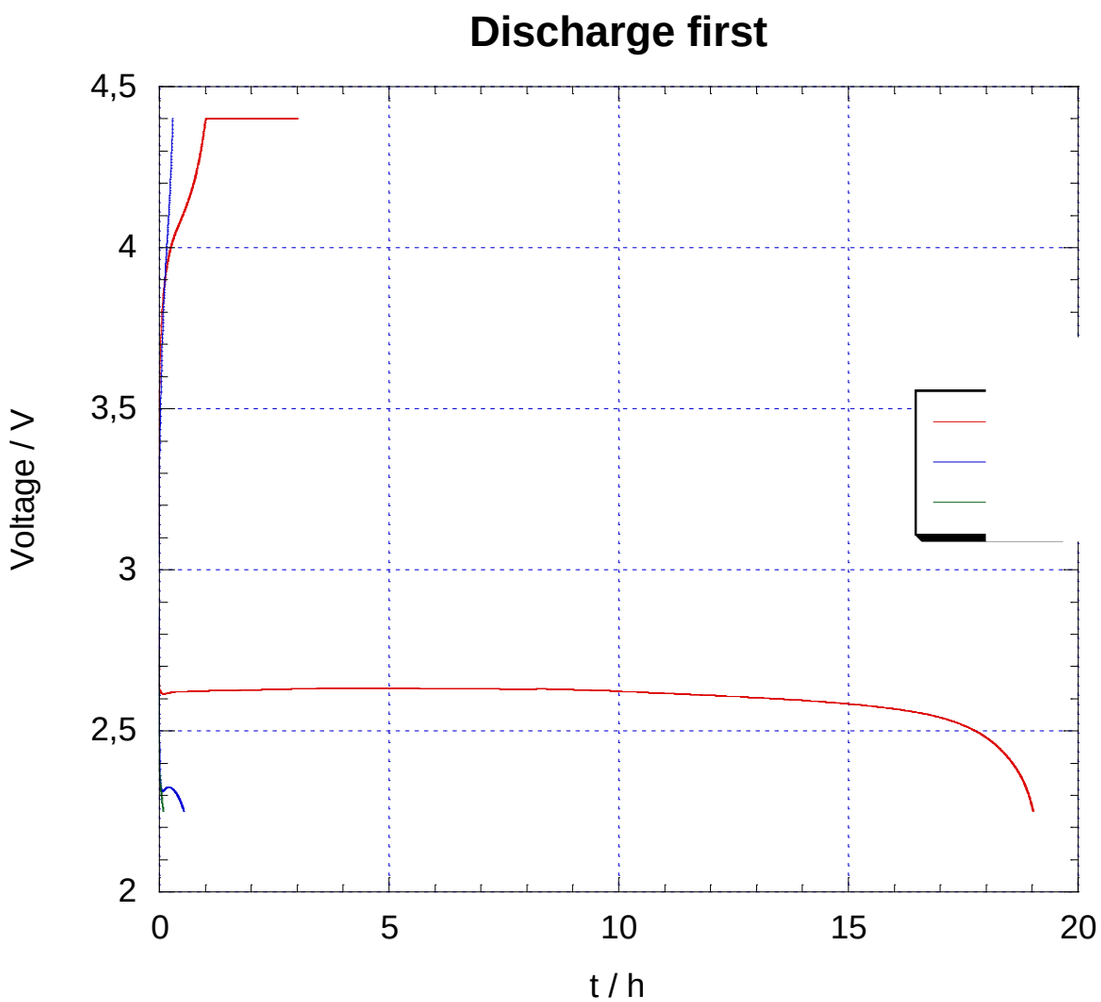
Voltage: 4.4-2.25 V
Charge/discharge: 2.5 mA
(0.1 mA cm^{-2})
Room Temperature: 23ºC
Dry Oxygen at atmospheric pressure

$q(O_2)$ = 30 mL min^{-1}
OCV with O_2 = 2.883V (after 3.5h)

Stable before discharge







Change of test conditions
(no time limitation):
1/ Complete discharge to 2.25V
2/ Recharge to 4.4V (CC+CV)

1st Discharge: 2.62V
19h → 47.5mAh
***1268 mAh/g** (1.5mg/cm²)*

Protective membrane

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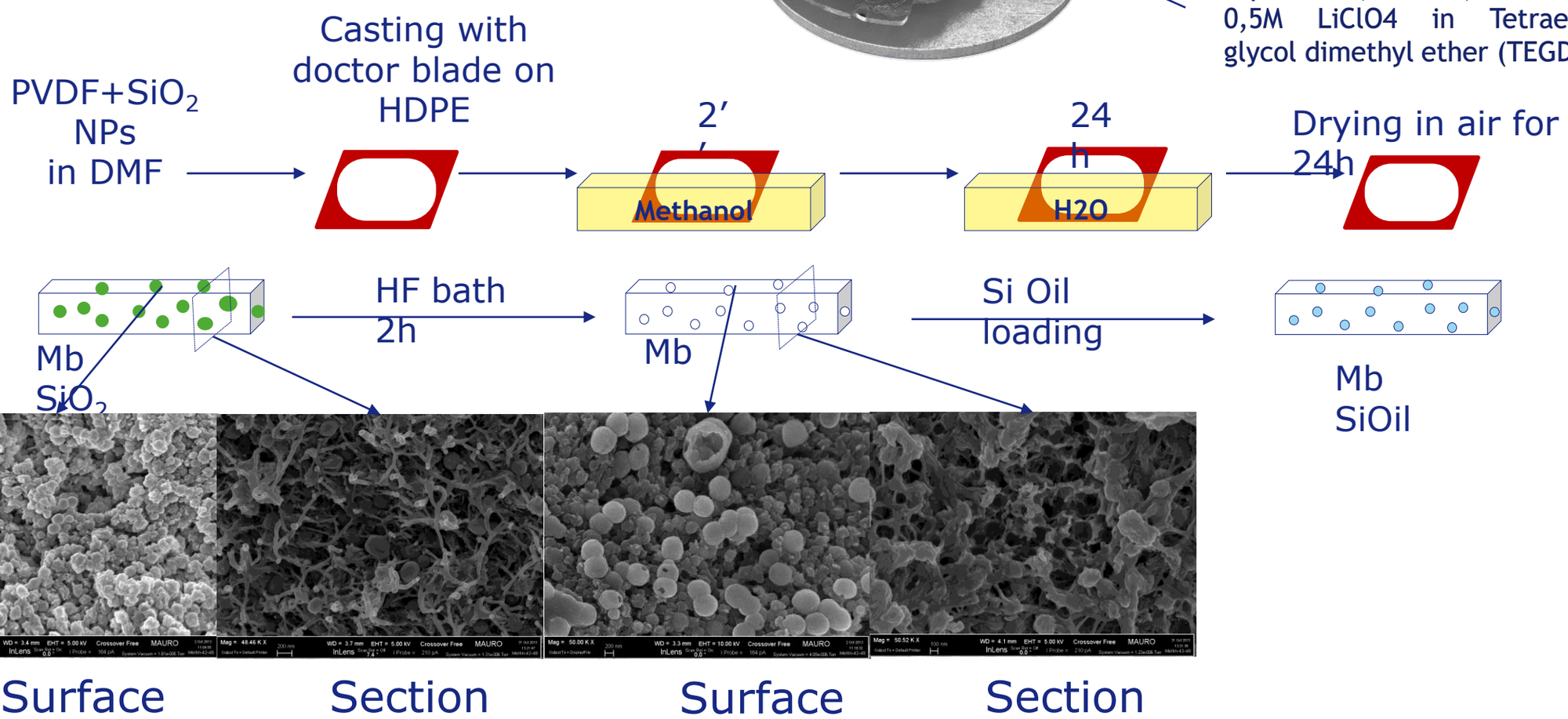
Membrane

Current collector

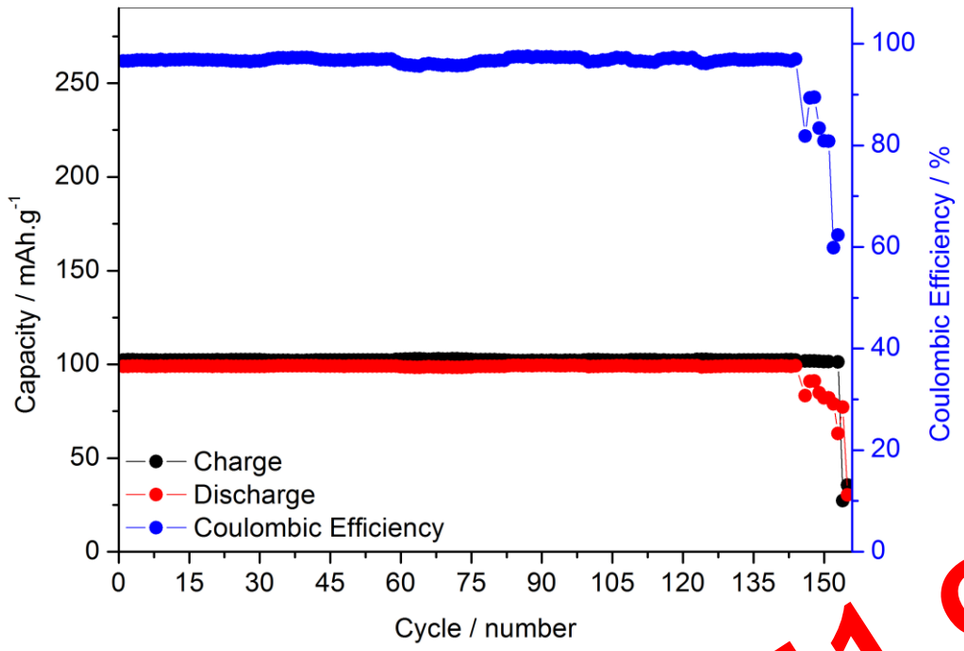
Cathode: GDL (SIGRAGET GDL-24BC with microporous layer).

Separator: ECC1-01-0012-A/L 18 mm x 0.65 mm glass fibre separator (EL-CELL) + Electrolyte: 0,5M LiClO4 in Tetraethylene glycol dimethyl ether (TEGDME).

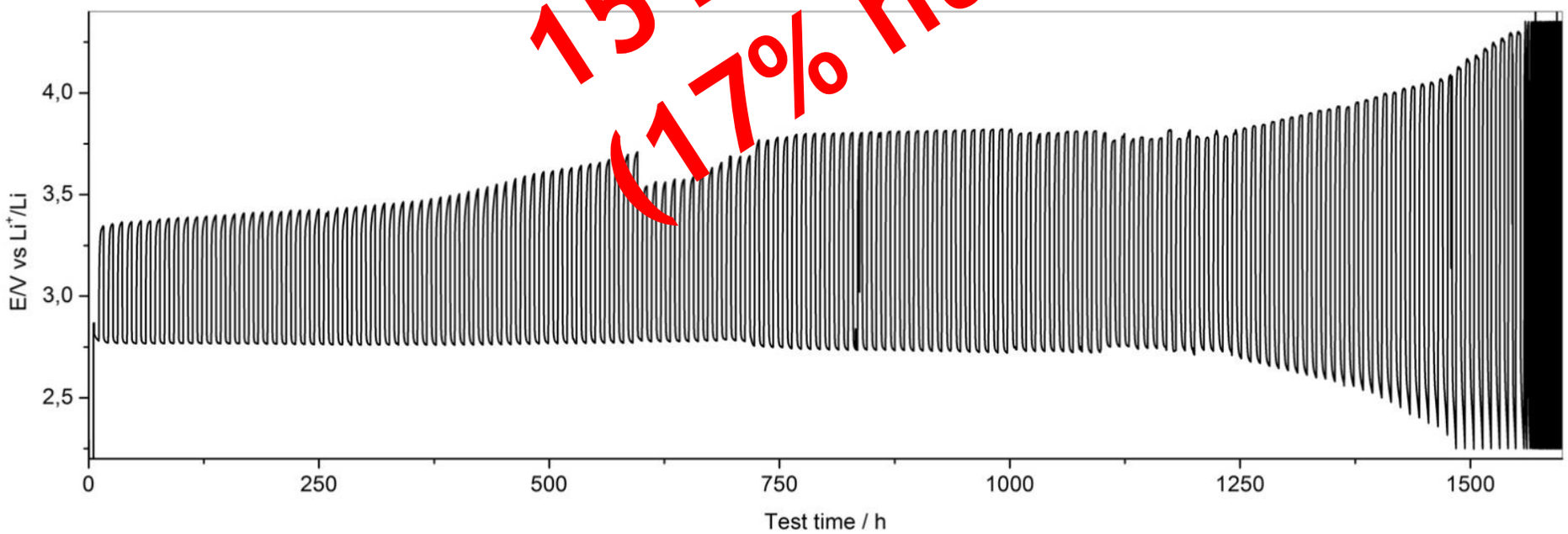


CHARACTERISTICS OF DEHYDRATION MEMBRANE			
$MbSiO_2$	**O_2 permeability**	**H_2O permeability**	**Contact angle**
	0,426 Barrer	733,246 [g/(m^2.24h)]	148,72 ± 16,4
Mb	0,940 Barrer	815,861 [g/(m^2.24h)]	93,5 ± 5,1
MbSioil	0,487 Barrer	28,875 [g/(m^2.24h)]	120,76 ± 11,6

Li-air cell prototype new membrane



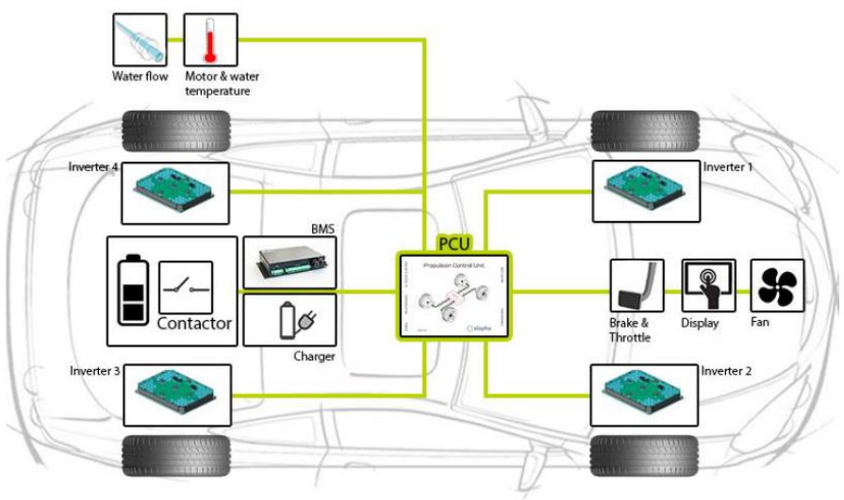
151 cycles in AIR
(17% humidity)



Future use of Li-air technology

Challenges for easier use of Li – air cells in the future EVs:

- Low power density expected (not necessary a problem)
- Unknown expected cycle life (humidity problem)
- Lower voltage then Li-ion cells (larger number of cells required)
- Wide voltage operation range (challenging system optimization)
- Required electronics (PCU) for charger, oxygen supply, BMS
- Cost and safety optimization



Conclusions

	Li-air	LiS	Na-ion	Li-ion
Specific energy	11140 Wh/kg (theor)	500 W·h/kg demonstrated	100-400 Wh/kg	100-300 Wh/kg
Energy density		350 W·h/L		250-700 Wh/kg
Charge/discharge efficiency	C/10 prototype	C/5 nominal		till 10C
Cycle durability	150	disputed	1000	1000
Nominal cell voltage	2,9 V	2,5-3 V	3 3.4 V	3,5 4.3 V

- Several issues need to be overcome
- Li-air can be realized without any Critical Raw Materials
- In order to use electrochemical batteries with low environmental impact with really high energy Li-air can become one solution
- Li-ion is a huge competition with Asiatic countries
- The competition on post-lithium ion is still open → **EC can help in this direction**

Thank you for your attention

To learn more about the STABLE project

www.fp7-stable.com